

AD-A168 646

SOME EXPERIMENTAL ARTIFACTS IN LEED STUDIES OF PHASE  
TRANSITIONS(U) MAINE UNIV AT ORONO DEPT OF PHYSICS AND  
ASTRONOMY W N UNERTL ET AL MAY 86 TR-11  
N00014-79-C-0441

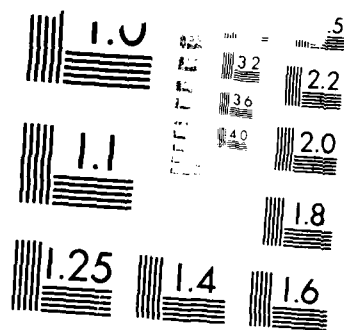
1/1

UNCLASSIFIED

F/G 20/2

NL





Viewing Distance: 100 cm

AD-A168 646

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report #11	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) SOME EXPERIMENTAL ARTIFACTS IN LEED STUDIES OF PHASE TRANSITIONS		5. TYPE OF REPORT & PERIOD COVERED Technical Report (1.2)
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) W. N. Unertl, D. E. Clark and C. S. Shern		8. CONTRACT OR GRANT NUMBER(s) Contract #N00014-79-C-0441
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Physics and Astronomy University of Maine, Orono, ME 04469		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Project #NR392-032
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Physics Program Office Arlington, VA 22217		12. REPORT DATE May 1986
		13. NUMBER OF PAGES 14
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)  Approved for public release; distribution unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)  DTIC ELECTRONIC S JUN 11 1986 A		
18. SUPPLEMENTARY NOTES  to be published in J. Vac. Sci. Technology		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)  Low Energy Electron Diffraction, Phase transitions, surface lattice dynamics, surface defects		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  see first paragraph		

DD FORM 1 JAN 73 1473

EDITION OF 1 NOV 65 IS OBSOLETE  
S/N 0102-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

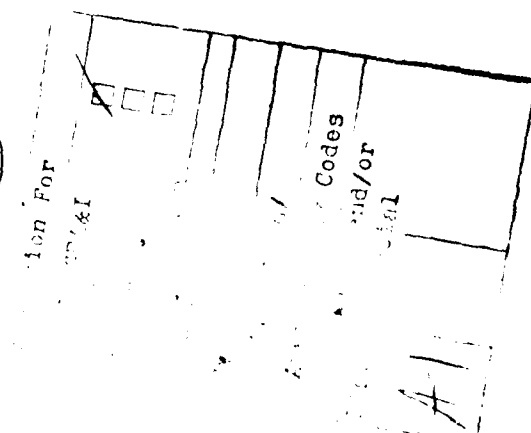
DTIC FILE COPY

SS FrA 4

SOME EXPERIMENTAL ARTIFACTS IN LEED  
STUDIES OF PHASE TRANSITIONS

ABSTRACT

Low energy electron diffraction, LEED, is an important experimental technique for the study of continuous order-disorder phase transitions. Extraction of the critical exponents and their associated amplitudes requires an accurate determination of the single-scattering intensity vs. parallel component of the scattering vector. Interpretation of measured intensities is complicated by multiple scattering, variation of the scattering factor, and thermal vibrations. These can cause the measured intensity profiles to be skewed and can add substantial intensity which is peaked at the Brillouin zone center. An example of subsidiary structure induced by multiple scattering is given for Au(110). The effects on the measured critical exponents  $\beta$ ,  $\gamma$  and  $\nu$  are shown to be small in most cases. However, the amplitudes associated with these exponents, such as the correlation length  $\xi$ , can be seriously affected. Some of these effects also occur in other diffraction methods.



Surfaces provide models of two-dimensional systems which have a rich variety of continuous, second-order phase transitions. There has been a recent, rapid increase in the use of low-energy electron diffraction, LEED, to study these transitions and the results of these studies are beginning to provide tests of the concepts of Universality and Scaling [1]. For example, the Au(110) (1x2) order-disorder transition is now known to belong to the Ising Universality Class [2,3]. A number of factors which influence the LEED intensities have not been accounted for in the analyses reported so far. This paper discusses two of these factors: multiple scattering and thermal diffuse scattering, TDS. These effects are not new [4,5] and the primary purpose of this paper is to discuss how they influence LEED studies of critical behavior.

The data required for analysis of critical properties consists of the intensity measured along a direction parallel to the surface. The variation of such a "spot profile" for temperatures near the critical temperature  $T_c$  contains the information needed to characterize the phase transition. For a continuous transition, the intensity in the profile is usually written in the form [1]

$$I(S_{\parallel}, T) = I_0(T) \delta(S_{\parallel} - G_{hk}) + \chi(S_{\parallel}, T) \quad (1)$$

where  $I_0(T)$  is the intensity due to long-range-order in the ordered phase and  $\chi(S_{\parallel}, T)$  is due to fluctuations occurring near  $T_c$ ;  $G_{hk}$  locates the reciprocal lattice rods,  $S_{\parallel}$  is the component of the scattering vector parallel to the surface;  $S_{\parallel} \equiv$

$k_{||} - k_{0||}$  where  $k_{||}$  and  $k_{0||}$  are the surface components of the scattered and incident wave vectors respectively. Near  $T_c$ , the quantities  $I_0$ ,  $\chi$  and  $\xi$  (the inverse of the width of  $\chi$ ) are predicted to have the following power law behavior[1-3,5]:

$$I_0 \approx A|t|^{2\beta} \quad (2a)$$

$$\chi(0,t) \approx \chi_0|t|^{-\gamma} \quad (2b)$$

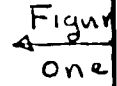
$$\xi(t) \approx \xi_0|t|^{-\nu} \quad (2c)$$

where  $\beta$ ,  $\gamma$  and  $\nu$  are the critical exponents whose values determine the universality class of the transition.  $\xi$  is also known as the correlation length.

Diffraction from a real surface is more complex than indicated by Equation 1, which neglects the angular and energy dependence of the differential scattering cross-section, the effects of multiple diffraction, and the effects of thermal vibrations. Each of these quantities depends explicitly on the scattering geometry. The latter two are also functions of temperature.

Finite size effects [6] due to extended or point defects, such as steps and impurities, can also influence the diffracted intensity but are not considered here. The important effects of instrumental parameters, some of which can be conveniently expressed in terms of a transfer function [7], are also not discussed here.

### 1. Experimental Geometries

Measurements of intensity profiles are usually carried out in one of the three geometrical configurations shown in Figure 1. The *constant energy* configuration,  Figure 1a, fixes  $k_0$  and the direction of  $\mathbf{k}$  is varied at constant  $E$ . This configuration

describes both the diffraction pattern observed visually on the screen of a retarding field analyser and the intensity measured with a movable Faraday collector. The *constant  $\theta$*  configuration, Figure 1(b), fixes the angle between  $\mathbf{k}$  and  $\mathbf{k}_0$  and  $E$  is varied. The constant  $\theta$  configuration is appropriate when a spot photometer is used to measure the intensity at a fixed point on the screen as a function of energy. The *constant  $S$*  configuration, Figure 1c, fixes the scattering angle between  $\mathbf{k}$  and  $\mathbf{k}_0$  and the crystal is rotated about the incidence direction. This configuration applies when the crystal is rotated with fixed detector position; the measured profile is a type of rocking curve. In each of the above cases, the intensity is not measured as a function of  $S_{||}$  but along some other trajectory in reciprocal space. The magnitude of  $S_{||}$  can of course be calculated from

$$S_{||} = 2\pi (E/150.4)^{1/2} (\sin\theta - \sin\theta_0)$$

where  $\theta$  is the exit angle and  $\theta_0$  the incidence angle, both measured with respect to the surface normal. The only technique which measures  $I$  vs  $S_{||}$  directly is Mirror-Electron-Microscopy-Low-Energy-Electron Diffraction, MEMLEED (2).

If the intensity along the reciprocal lattice rod has structure such as that caused by multiple scattering, each of the experimental configurations in Figure 1 will lead to an incorrect determination of the angular profile. This is illustrated schematically in Figure 2. The upper panel shows intensity contours around an intensity maximum on a reciprocal lattice rod. The dashed line represents the trajectory of the measurement and the horizontal line is the desired trajectory for analysis using Equation 1. In the lower panel, the measured angular profile (dotted curve) and the true profile are shown. For the case shown in Figure 2, the widths of

Figure  
Two

the profiles differ by a factor of two. Near a continuous phase transition, the width of the line profile, Equation 2c, changes as the temperature is varied near the critical temperature  $T_c$ . At  $T_c$ , the profile is very narrow and the contours in Figure 2 become more elongated causing the error in profile measurement to be reduced. Away from  $T_c$ , the contours become more circular leading to a larger error in profile width measurement. The net result is a temperature dependent overestimate of  $\xi$ .

Fortunately, it is simple to correct for this effect: Each intensity point  $I(S_{||}, S_{\perp})$  on the measurement trajectory must be normalized to the intensity measured on the reciprocal lattice rod at the same  $S_{\perp}$ . To do this, the inner potential must be known, but a several eV uncertainty has only a small effect.

The discussion in Section 2 provides a specific example for the case of a line profile measurement on the Au(110)(1x2) surface. The uncorrected profile with maximum at 62 eV, Figure 2a, is ten percent narrower than the corrected profile, Figure 2c.

## 2. Multiple Scattering

It is well established that multiple scattering is very important in LEED [5] and results in significant modulation of the diffracted intensities. Most experimental studies of phase transitions have attempted to minimize multiple scattering *within* surface layer by using normal incidence since the differential scattering cross section has its minimum value when the scattering angle is near ninety degrees. However, multiple scattering with the substrate always occurs even in the simplest two beam approximation [5]. In the absence of multiple scattering, the intensity scattered from a 2D system would change smoothly with  $S_{\perp}$ , with the only variations due to the differential scattering cross section and the thermal diffuse



scattering. A glance at actual intensity profiles such as that for Au(110) in Fig. 3b shows that significant modulation is the rule. Thus, LEED can only be a useful tool for quantitative studies of phase transitions if multiple scattering has unimportant effects on the spot profiles. Most LEED studies have tacitly assumed this to be the case. However, whether this is ever true remains to be demonstrated. In fact, calculations which simulate the effects of disorder on the multiple scattering show that the intensity profiles can be altered [8].

An example on multiple scattering effects is shown in Figure 3 for the  $(0, -0.5)$  beam of Au(110)  $(1 \times 2)$ . The line profile shown in Figure 3a was obtained in the constant  $\bar{\theta}$  configuration, Figure 1b. Instead of the profile being a simple, nearly symmetrical peak with maximum at 62 eV, additional structure is apparent near 45 eV. The center panel of Figure 3 shows the intensity measured along the reciprocal lattice rod. None of the fine structure between 40 and 85 eV can be explained by a single scattering analysis based on the known structure of this surface [9]; it is due to multiple scattering. The additional structure in the spot profile is caused by the large peak at 45 eV in Figure 3b. If the assumption is made that multiple scattering does not influence line shapes measured as a function of  $S_{||}$ , then this multiple scattering induced structure will be removed by dividing the profile measurement of Figure 3a by the intensity of Figure 3b as described in conjunction with Figure 2. The result of this normalization is shown in Figure 3c and eliminates most but not all of the subsidiary features. The remaining sharp structure at 51 eV must be due to breakdown of the assumption that the multiple scattering does not vary with  $S_{||}$ . It cannot be due to incorrectly accounting for thermal diffuse scattering as discussed in the next section since failure to correct for TDS would produce a dip rather than a peak.

Several approaches are needed before it will be possible to better understand the

Fig  
Th

relative importance of multiple scattering in intensity profile measurements. First, multiple scattering is a strong function of geometry. Thus, if spot profiles are measured for a wide range of experimental parameters, the critical exponents extracted from them will not be the same if multiple scattering contributions are significant. Such measurements have not been reported. The second approach is to compare LEED profiles with profiles obtained by glancing incidence x-ray diffraction, for which multiple scattering effects are not important. Finally, theoretical calculations of the effects of multiple scattering on spot profiles need to be carried out for both ordered and disordered systems. Computational methods needed for such a study are currently under development (8).

It should also be pointed out that the method of Bartelt, Einstein and Roelofs (3,10) for determination of the specific heat critical exponent  $\alpha$  does not seem to be sensitive to multiple scattering effects.

### 3. Thermal Diffuse Scattering

The effects of thermal diffuse scattering TDS due to vibrations of the scatterers about their rigid lattice sites has also been left out of Equation 1. In general TDS redistributes intensity throughout the Brillouin zone. Because the diffracted intensity from a surface is distributed along a reciprocal lattice rod rather than isolated at reciprocal lattice points, TDS is substantially more important for diffraction from surfaces than for diffraction from the bulk (11).

For a surface which does not undergo a phase transition, the TDS is conveniently described in terms of three components, each with a different  $S$  and  $T$  dependence (4,11). In the high temperature limit, the zero-phonon, or Bragg intensity  $I^{(0)}$  is the rigid lattice intensity reduced by the Debye-Waller factor:

$$I^{(0)} = I_0 e^{-2MT} \quad (3)$$

where  $2MT \equiv \langle (S \cdot u)^2 \rangle$  for single scattering. Here  $u$  is the instantaneous displacement of an atom from its lattice site and  $\langle \dots \rangle$  represents a thermal average. The one-phonon intensity  $I^{(1)}$  is due to scattering events which involve a single phonon and is peaked near the center of the Brillouin zone. Its  $T$ -dependence is given by:

$$I^{(1)} \propto 2MT e^{-2MT}. \quad (4)$$

Higher order phonon scattering gives rise to the multiphonon intensity  $I^{(m)}$  which is nearly uniformly distributed throughout the Brillouin zone and has  $T$ -dependence

$$I^{(m)} \propto 1 - e^{-2MT} - 2MT e^{-2MT}. \quad (5)$$

Combination of the analysis leading to Equations 3-5 with that leading to Equation 1 plus the assumption that the time scale for thermal vibrations to reach equilibrium is much shorter than the time scale of the critical fluctuations shows that the TDS has the same general effect on the critical scattering  $\chi(S, T)$  as it does for the Bragg scattering [3, 12]. The integrations over the phonon wave vectors required to evaluate these effects quantitatively are complex and cannot be carried out analytically. Furthermore, the variation of  $u$  near a phase transition is not known. This makes it impossible at present to directly calculate the effect of one phonon scattering on the angular profile of  $\chi(S, T)$ . However it is possible to draw some qualitative conclusions.

First, the  $T$ -dependence of the TDS near  $T_c$  is slow compared to that due to the fluctuations. Expansion of Equations 3-5 in powers of reduced temperature  $t$  about

$T_c$  shows that the critical exponents will be in error by only a few parts per thousand for realistic values of  $2M$  and  $t < 0.1$ . This is well within the uncertainty with which the exponents can currently be determined. However, such errors could begin to be important in studies of both finite size effects and higher order correction terms to the exponents.

Second, the TDS intensity always adds a term to the measured intensity which is peaked near the Brillouin zone center. Thus, the amplitudes associated with each of the critical exponents in Equation 2 will be increased by the addition of a temperature dependent term if no correction is made. For example, if the TDS behavior measured for Ag(111) [12] is assumed be approximately correct for Au(110) (1x2) near  $T_c$ , these effects are found to be as large as twenty percent. Since the amplitudes are not universal quantities but depend upon the specific physical model, the ability to experimentally test each model will be limited unless the effects of TDS are better understood.

#### 4. Summary

In summary, some corrections to LEED lineshape analysis have been discussed which limit the accuracy with which the critical behavior of a continuous, order-disorder phase transition can be studied. Multiple scattering is shown to influence the measured lineshape. Thermal diffuse scattering has only a small effect on the extraction of critical exponents but causes significant errors in the associated amplitudes.

These results are also expected to hold for reflection high energy electron diffraction, RHEED, and the results concerning thermal diffuse scattering should be valid for glancing incidence x-ray diffraction.

## 5. Acknowledgements

This work has been supported in part by the Office of Naval Research and the National Science Foundation (DMR 8020840). Useful discussions with P. Kleban are acknowledged.

## 6. References

1. L. D. Roelofs, *Appl. Surf. Sci.* **11/12** (1982) 425.
2. J. C. Campuzano, M. S. Foster, G. Jennings, R. F. Willis, and W. N. Unertl, *Phys. Rev. Lett.* **54** (1985) 2684.
3. D. E. Clark, Ph.D., University of Maine, 1985, unpublished; D. E. Clark, C. S. Shern and W. N. Unertl, to be published.
4. M. B. Webb and M. G. Lagally, *Sol. State Phys.* **28** (1973) 301.
5. J. B. Pendry, Low Energy Electron Diffraction, Academic Press, New York, 1974.
6. P. Kleban in Chemistry and Physics of Solid Surfaces V, ed., R. Vanselow and R. Howe, Springer-Verlag, Berlin, (1985) 339.
7. R. L. Park, J. E. Houston, and D. G. Schreiner, *Rev. Sci. Instr.* **42** (1971) 60.
8. J. B. Pendry in The Structure of Surfaces, ed. M. A. Van Hove and S. Y. Tong, Springer-Verlag, Berlin (1985) 124; W. Moritz, (private communication).
9. I. K. Robinson, *Phys. Rev. Lett.* **50** (1983) 1145.
10. N. C. Bartelt, T. L. Einstein and L. D. Roelofs, *Phys. Rev. B* **32** (1985) 2993.
11. M. G. Lagally in Surface Physics of Materials, ed., J. M. Blakely, Academic Press, New York (1975), vol. II, 419.
12. R. L. Dennis and M. B. Webb, *J. Vac. Sci. Tech.* **10** (1973) 192.

### Figure Captions

Figure 1: Experimental geometries for line profile measurements.

- a. Constant  $E$ : The incident wave vector  $\mathbf{k}_0$  is fixed and the scattered wave vector  $\mathbf{k}$  is moved along the Ewald sphere as shown by the dashed line.
- b. Constant  $\theta$ : The directions of  $\mathbf{k}_0$  and  $\mathbf{k}$  are fixed and  $E$  is varied. The trip of the wave vector  $\mathbf{k}$  moves along the straight dashed line.
- c. Constant  $S$ :  $\mathbf{k}_0$  and  $\mathbf{k}$  are varied to move the tip of  $\mathbf{S}$  along the dashed circle centered on the origin.

Figure 2: The effect of intensity variations along a reciprocal lattice rod on measured line profiles. The upper panel shows intensity contours near a maximum in the intensity. The dashed line shows the trajectory of the measurement; see Figure 1. The lower panel shows the line profile measured by experiment (dashed line) and the true line profile (solid line) measured along  $S_{\parallel}$ .

Figure 3: Intensity measurements for Au(110)(1x2).

- a. Line profile measured in the constant  $\theta$  configuration shown in Figure 1b.
- b. Intensity vs energy profile measured along the  $(0, -1/2)$  reciprocal lattice rod.
- c. Line profile from a divided by the intensity profile b at equal values of  $S_{\perp}$ .

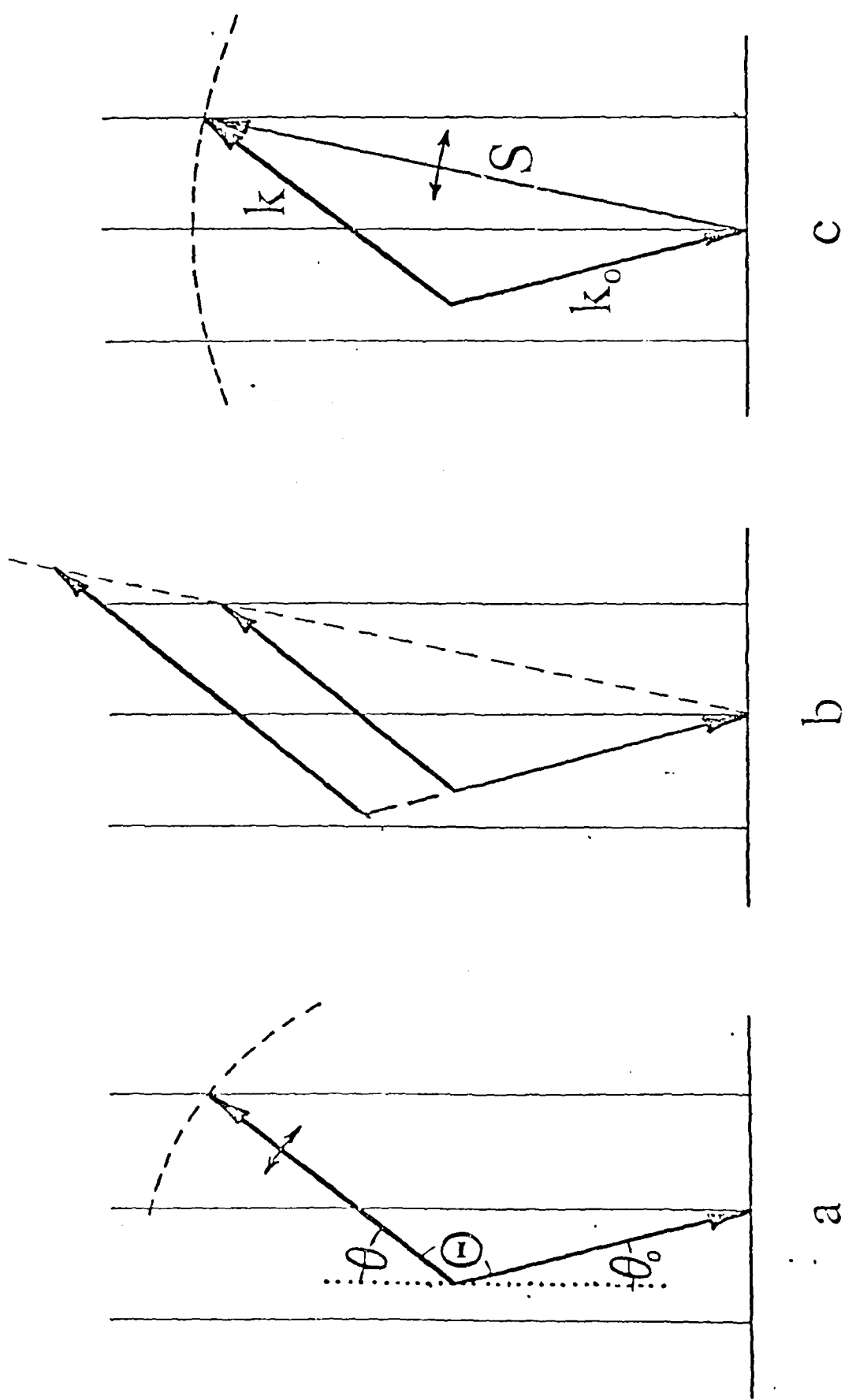
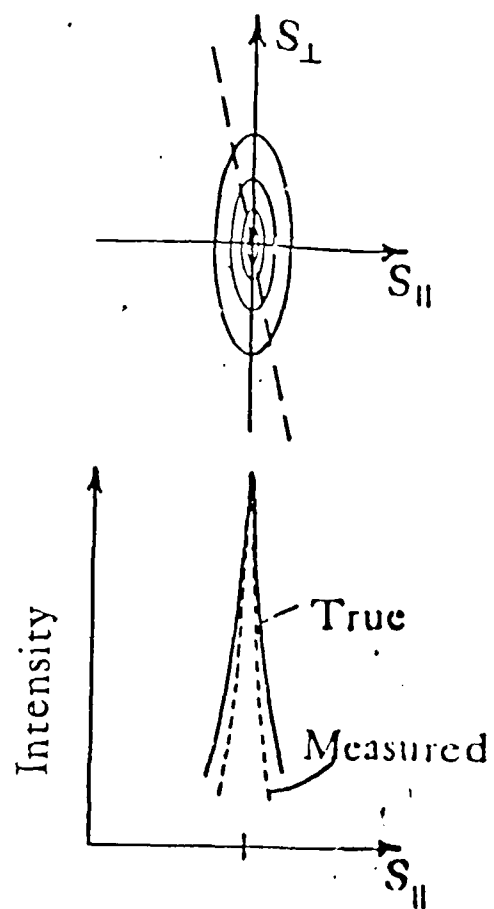


Figure 1





NORMALIZED INTENSITY

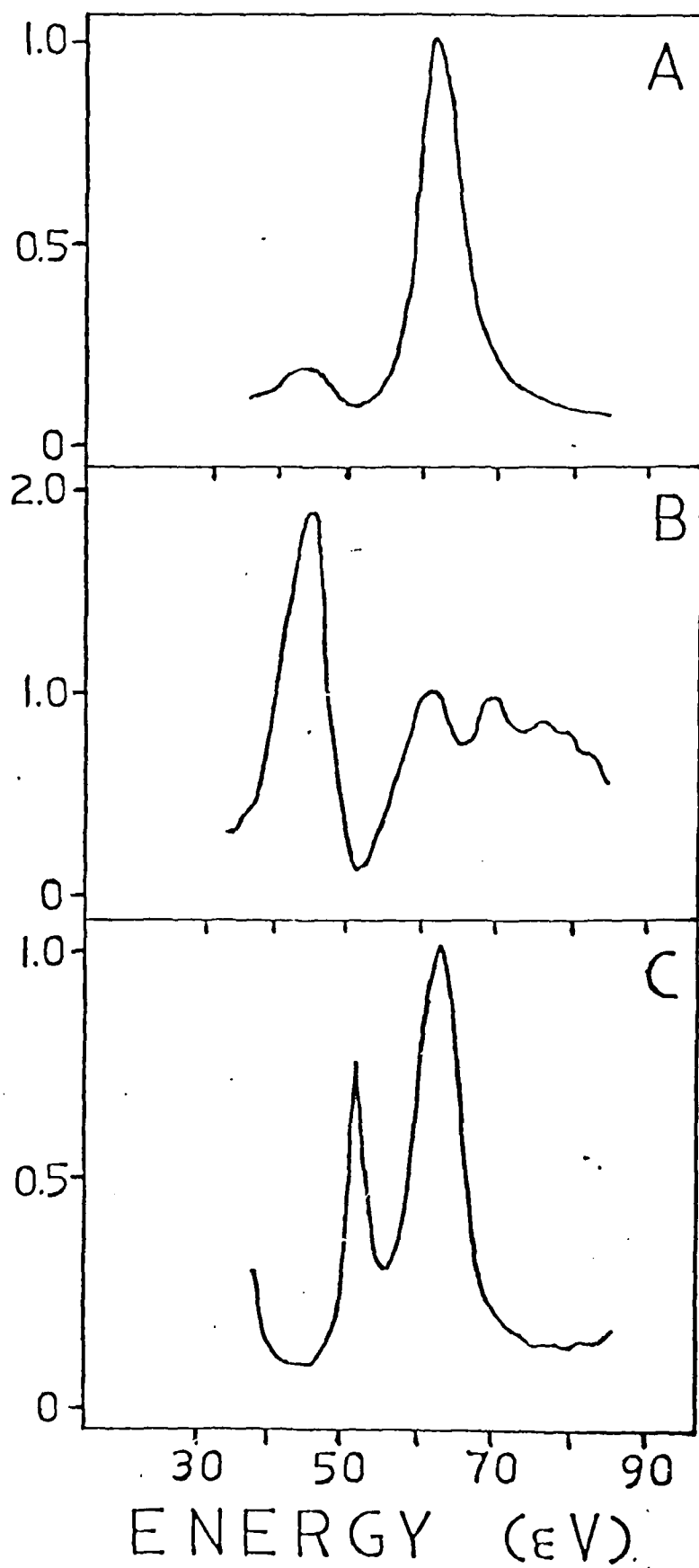


FIGURE 3

END

Dtic

7-86